THE CRYSTALLITE SIZE, IONIC CONDUCTIVITY, AND DIELECTRIC CONSTANT OF CHITOSAN-MILLED

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ABSTRACT

The effect of milling time on the crystallite size, ionic conductivity, and dielectric constant of chitosan-milled had been investigated. The chitosan-milled was fabricated using ball milling with the various time were 0, 60, 180 and 360 minutes, indicated by CHO, CH60, CH180 and CH360, respectively. From the XRD results, the milling time not only resulted in the homogenous dispersion but also the reduction of particle clustering and the reduction of distances between the particles. The chitosan-milled showed that the milling time contributed on the crytallite size. The average crytallite size of chitosan nanopowder were 20 nm. The dielectric constant and loss values decreased with the frequency and increased with the milling time. Finally, the effect of milling time on crytallite size, ionic conductivity, and dielectric properties of chitosan-milled could increase the internal structure of the granules and applied to synthesis the solid electrolyte battery.

Keywords: crytallite size, ionic conductivity, dielectric constanst, chitosan-milled

INTRODUCTION

Chitosan is one of the organic biopolymer materials processed with deacetylation of chitin that is polymerization of glucosamine chains (2-amino-2-deoksi-β-(1-4)-D-Glukosa) and has a molecule formula $[C_6H_{11}NO_4]_n$ with a molecular weight is 2,5 x 10^5 Dalton. Characteristic of chitosan is non-toxic, biodegradable, and hydrophilic. Chitosan has an amine and hydroxyl functional group (Abdulla et al., 2017; Kartika et al., 2020). Synthesis of chitosan obtained from animal shells like shrimp, crab, lobster (Kartika et al., 2018). Chitosan is formed in yellow-white powder, has no smell, and has no taste. Chitosan is more attractive to develop because of the existence of an amine group so that chitosan can dissolve in acid that can be used for the synthesis of membrane or fiber (Zhang et al., 2014; Rochima et al., 2016). Also, the particle size of chitosan can be formed to nano and the surface area is small so it can easily be modified by other chemical materials (Liu et al., 2011; Zhan et al., 2014; Ker et al., 2000).

Ball milling is a common mechanical process to produce surperfine powders. It is used to get the nano-sized particles such as starch, cellulose, and chitosan. The chitosan nanopowder is widely used for further research. The mechanical milling method is one of milling method for reducing particle size, some physicochemical properties and structure of chitosan will change and influence its performance.

According to the literature, preparation and characterization of chitosan nanopowder and its properties using ball milling obtained a great part of particles had sizes in micrometers are successufully synthesized using the ball milling. The chitosan properties can be synthesized to study the effects of biocompatibility and biodegrable. The influence of plygonum minus by ball milling can be reduced the particle size. The preparation of nano-sized chitosan using ball milling treatment with a variety of milling time have been investigated and indicated that the average of grain size is 15.1 nm. Dielectric properties showed that ion conduction mechanism between electrode and electrolyte are very important for electrochemical devices.

However, there were few research of as-prepared chitosan by ball milling with various milling time. The synthesis of chitosan-milled using ball milling may offer new possibility for the chitosan nanopowder applications because of the process is very simple, low cost and highly surface area that is high yield. Although, in fact, using of the ball milling to prepare the chitosan nanopowder is still done with several challenges, such as the large average size range of the as-prepared chitosan, in this study would get different results beyond the theme. Analysis some efforts for the development of as-prepared chitosan that were applied by the mechanical treatment to get smaller particles, to reduce grain size and surface modification of chitosan through ball milling. This study will focus on the effect of milling time on microstructure and dielectric properties of chitosan nanopowder. This work is started by preparation of the chitosan nanopowder by ball milling with different milling time. The crystallite size, ionic conductivity, and dielectric properties of the chitosan-milled are also discussed as well.

MATERIAL AND METHODS

The research was conducted in the Laboratory of Material Physics Department of Physics Jenderal Soedirman University and Laboratory of Organic Chemistry Gadjah Mada University from April to August 2021. The prepared chitosan (CH0) was purchased from Biotech Surindo (Cirebon, Indonesia) with a deacetylation degree (DD) about 85%. The CH0 was conducted to the processed to be nano-sized chitosan CH60, CH180 and CH360, with the milling time of 60, 180 and 360 minutes, respectively.

A high-energy milling machine 8000M SPEX CertipPrep Mixer/Mill here was used. The jars and the milling medium were made of stainless steel. The diameter of small ball is 0,5 mm. The time for grinding operations were 60, 180 and 360 minutes and rotated at the constant speed 1500 rpm and its rotational direction every on 1 h and off 30 min for every experiment continuously. The milling process was done by means of a planetary ball milling with some parameters with respect to size reduction. After milling, the dried samples were ground for 10 minutes and then characterized.

Crystal structure of CH0, CH60, CH180 and CH360 were performed using X-ray Diffraction (XRD) tyoe Rigaku D/max 2500 V diffractometer (Rigaku, Japan) with the Cu-Kα radiation with λ = 1.54060 Å, 40 kV, 30 mA, divergence slit/scattering slit, and 0.3 mm receiving one.

The ionic conductivity, and dielectric properties of CH0, CH60, CH180 and CH360 were pelletized into 15 mm diameter spherical forms using 15 Mpa uniaxial pressures. Impedance spectra were collected at an applied of 1 V and frequency range of 42 Hz – 5 MHz using HIOKI LCR HiTESTER 3532-50.

RESULT

Figure 1 shows the XRD patterns for CH0, CH60, CH180 and CH360. The XRD phases of the CH0, CH60, CH180 and CH360 were indetified with the standard Joint Committee on Powder Diffraction Standards (JCPDS Card No. 39-1894).

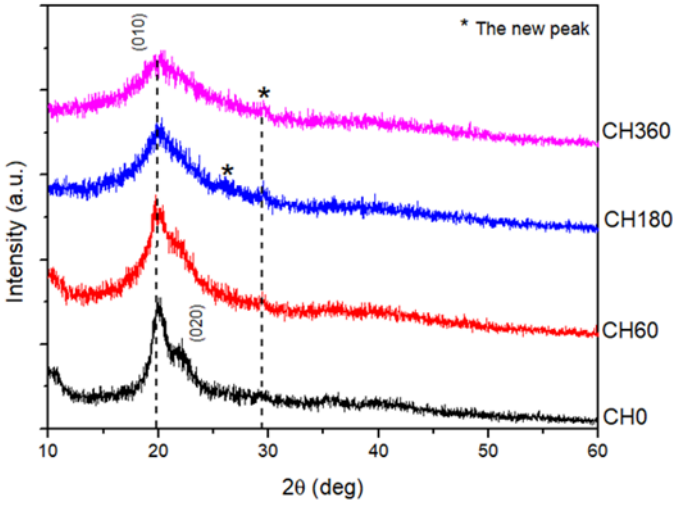


Figure 1. XRD patterns of CH0, CH60, CH180 and CH360

In the Figure 1 shows that the two peaks of CH0 (2θ = 210 and 110) were assigned to (001), (100) and (101) crytallographyc planes, respectively. The crystallite size and crystalline degree were 20.8 nm and 49%. Polidispersity index is 44%. The peaks of CH60 were at about 210 and 110. The crystallite size and crystalline degree were 20.1 nm and 36%. Polydispersity index was 36%. The XRD pattern of CH180 and CH360 showed the peaks at 200 and 110. The crystallite size and crystalline degree of CH180 and CH360 were 20.1 nm. Polydispersity Index was 17%. The milling process decreased crytallite size and crytallite degree, but significantly increased the polydispersity Index. The crystallite size and grain size of CH0, CH60, CH180, and CH360, respectively as shown in Figure 2.

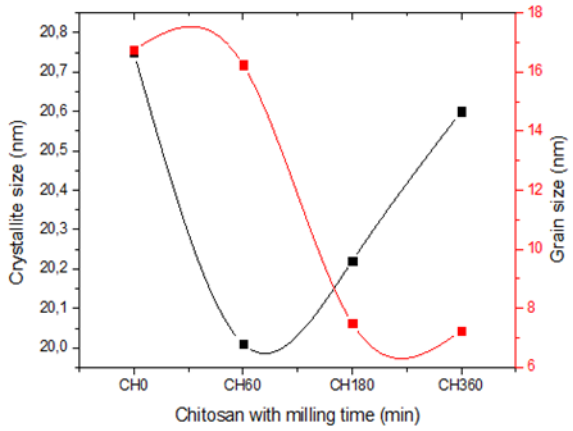
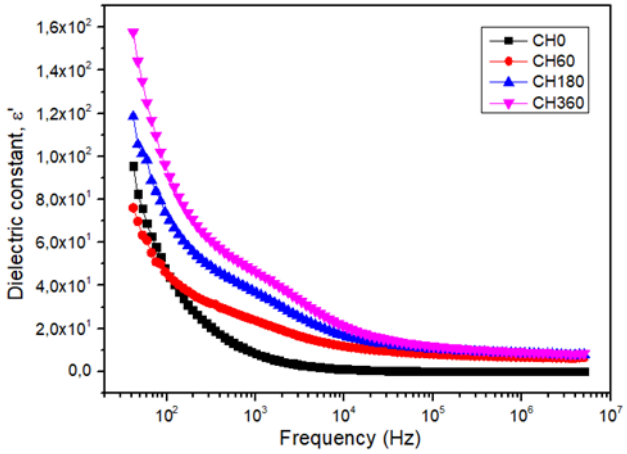


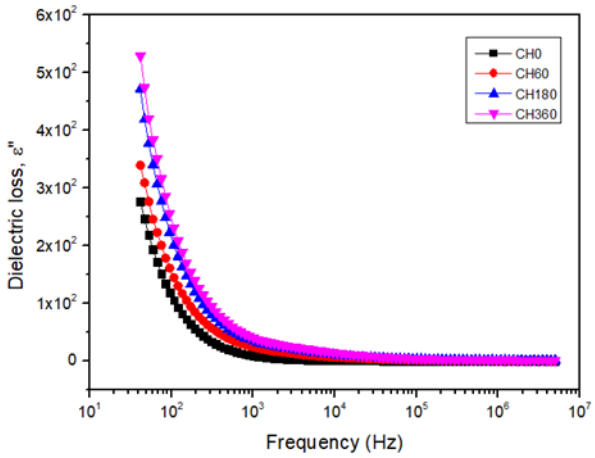
Figure 2. Milling time dependent the crystallite size and the grain size of CH0, CH60, CH180 aand CH360

Figure 2 depicts crytallite size and grain size of CH0, CH60, CH180 and CH360. The crystallite size decrease while the grain size indecrease as a function of milling time. The results indicate the particles are highly agglomerated and relatively dispersed. The particle were highly agglomerated and relatively dispersed because in the milling process was done, some parameters can influence the material particle size distribution and balls are typically larger and heavier. They can reduce the empty spaces and heat between the milling elements increasing the friction between the balls and the particles.

The real part of complex permittivity is the dielectric constant (ε^') and the imaginary part is the dielectric loss (ε^"). Variation of the dielectric constant and dielectric loss as a function of frequency at various milling time for chitosan can be seen in Figure 3(a) and (b).



(a)



(b)

Figure 3. Frequency-dependent plot of permittivit for CH0, CH60, CH180 and CH360, (a) dielectric constant, (b) dielectric loss at RT

Figure 3 (a) and (b) show the real and imaginary plot of permitivity for CH0, CH60, CH180 and CH360, respectively. The electromagnetic absorption of a material depends on the dielectric properties which are related to the complex permittivity (ε^' and ε^'') and permeability (μ). The frequency dependence dielectric constant indicates a continuous increase the dispersion at higher frequency. while the results of the dielectric constant of chitosan powder with variations in milling time consisting of dielectric gain and dielectric loss Adalah The real part of dielectric constant or dielectric gain (ε') and the imaginary part is the dielectric loss (ε"). Dielectric gain and loss showed that a very strong dispersion in the low frequency. The decrease of the ε' and ε' with the increase of frequency is due to the contribution of the charge polarization and the migration of ions between the electrode and electrolytes in the material. The dielectric constant parameters for the higher frequency showed that the increase of the milling time may be revealed to one of the sources of ion conduction.

CONCLUSION

Based upon this study, the effect of milling time on crystallite size, ionic conductivity, and dielectric properties of chitosan-milled have been conducted. Synthesis of the chitosan nanopowders with various milling time have been done using ball milling treatment. The XRD patterns showed the crystallite size is about 20.1 nm. From the SEM image and XRD pattern, it showed that chitosan nanopowder is easily agglomerated so as to produce cavities between granules and the size of the granules. The dielectric constant and the dielectric loss for all the samples show a relatively high value at low frequency and it decrease with increasing frequency. The dielectric constant values for the higher frequency showed that the increase of the milling time may be revelead to one of the sources of ion conduction. It can be concluded that the effect of milling time can decrease the crystallite size and the grain size of chitosan nanopowder. With increased the milling time, the high values of dielectric constat confirmed the high frequency

applications.

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